



Review

Homogeneous photo-Fenton processes at near neutral pH: A review

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ABSTRACT

The occurrence of new emerging contaminants in surface waters has recently grabbed increased attention of the scientific community. The adoption of Advanced Oxidation Processes (AOPs) represents an efficient strategy to remove recalcitrant compounds from aqueous streams and achieve high mineralization levels. Amongst AOPs, the photo-Fenton process has been widely investigated due to the possibility of using a renewable energy source (i.e., solar energy) and low concentration of catalyst. On the other hand, the use of photo-Fenton process is restricted to acidic pH values, with associated high operating costs for industrial scale applications. To overcome these drawbacks, photo-Fenton processes modified by adding selected chelating agents can be successfully performed at neutral pH. The present review aims at examining and comparing the most relevant papers dealing with photo-Fenton processes at neutral pH that appeared in the literature so far. Such papers were classified by chelating species adopted. In particular, for each iron(III)-ligand complex, the mechanism of photolysis, the speciation diagram, the light absorption properties, the quantum yields, biodegradation and toxicity, and some example of applications are reported. As a conclusion, suitable criteria for choosing chelating agent and operating conditions in photo-Fenton processes at neutral pH are proposed.

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1. Introduction

In recent years, many new contaminants found in municipal effluents and surface water have rightly attracted the attention of the scientific community [1,2]. Most of these contaminants occur in the environment at very low concentration but concerns exist regarding their possible bioaccumulation and persistence in the environment [3–6]. Several indications about difficulties in removing these contaminants by means of the most commonly used wastewater treatments are reported [7–12]. When no complete removal of certain species can be ensured, conventional wastewater treatment plants themselves become major sources of water pollution [13,14]. To overcome this issue, additional strategies, such as tertiary treatments, should be adopted. Amongst the various tertiary treatments, Advanced Oxidation Processes (AOPs) are considered capable of oxidizing different classes of organic pollutants and achieving high levels of mineralization [3].

The photo-Fenton process is one of the most studied AOPs and appears as an attractive alternative for removing emerging contaminants. The simplified reaction sequence leading to hydroxyl radical generation from hydrogen peroxide in photo-Fenton processes is identified by reactions r_1 and r_2 , as follows:

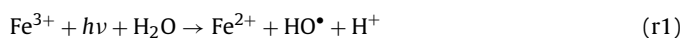
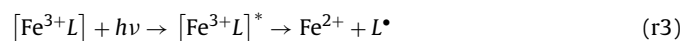


Photo-Fenton processes are reported to be effective in removing several classes of contaminants, such as pesticides [15,16], dyes [17,18], insecticides [19], pharmaceuticals [20], nitrobenzene [21], chlorophenols [22], and polychlorinated biphenyls [23]. Furthermore, the possibility of employing solar energy in photo-Fenton processes helps improving their economic and environmental sustainability.

However, the application of such processes implies some drawbacks including the need to operate in a narrow pH range (2.8–3.5). A strict pH control is substantially required to ensure that Fe(II) and Fe(III) species exert their catalytic role, thus avoiding any precipitation of inactive iron oxyhydroxides and maximizing the concentration of photoactive species. To this purpose, real applications include addition of acidifying reagents and final neutralization with relevant environmental and economic disadvantages [24]. Therefore, the possibility of working at neutral or near neutral pH aroused great interest in the research community. For example, several studies conducted at near neutral pH by harnessing the benefits of natural organic matter (NOM) on photo-Fenton systems were found [25–29]. In particular, Georgi et al. [26] examined the effect of the adding humic acid to an aqueous solution containing an organic species (benzene) in the pH range of 5.0–7.0. Rate values for the oxidation of benzene were as high as those measured at pH 3.0 in absence of humic acid.

The low efficiency affecting photo-Fenton processes at neutral pH is mainly due to iron precipitation, and can be therefore prevented by properly adding iron complexing agents. As pointed out in reaction r_3 , such compounds (L) should be able to form stable

complexes with Fe(III), which (i) significantly absorb UV–vis light and (ii) undergo photochemical reductions leading to Fe(II) ions.



Polycarboxylates and aminopolycarboxylates can form stable complexes with Fe(III), absorb light in the near-UV and the visible regions more efficiently than aquo-complexes [30,31], and undergo photoreduction through a ligand-to-metal charge transfer (LMCT) generating Fe(II) ions [32].

Since poor concentrations of complexing agents are usually found in industrial and civil wastewaters, their addition is required to efficiently perform modified photo-Fenton Processes [33–36]. The use of additional xenobiotic species, although optimizing the overall process, implies that a prior assessment of some of their properties, such as biodegradability and ecotoxicity, should be performed with the aim of selecting environmentally sustainable compounds.

It is worth noticing that removing acidification and neutralization phases along with their cost results into ample opportunity to employ photo-Fenton processes in large-scale applications [37].

This paper aims at performing a critical review of the literature, in which titles dealing with “photo-Fenton process at circum-neutral pH” are increasingly reported. For each organic ligand considered, an overview on the most relevant properties, such as types of complexes formed, UV–vis absorption, quantum yield of photolysis, biodegradability, and ecotoxicity is reported.

1.1. Relevance of the topic and limitations of the present work

A recent literature survey indicated an increased activity in the field of photo-Fenton processes at near neutral pH, with more than 30 papers published in the last 15 years (Fig. 1), thus attesting to the importance of this topic in wastewater treatment. In particular, the search was restricted to papers concerning intentional addition of specific ligands, in order to extend wastewater treatments to near neutral or neutral pH conditions. All papers investigating the effect of naturally occurring ligands (e.g., humic acids) or ligands formed during wastewater treatments (i.e., short carboxylic acids) were

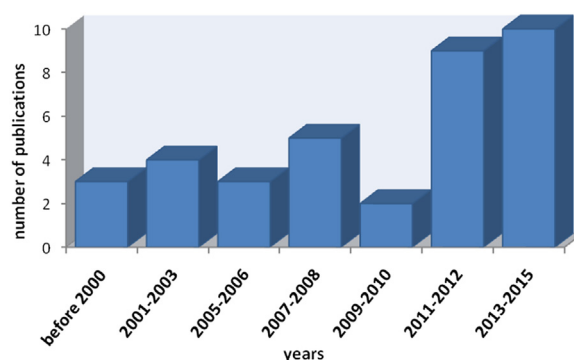


Fig. 1. Productivity of scientific papers on photo-Fenton processes at neutral pH (data sources: Scopus, ScienceDirect, Thomson Reuters Web of Science).

Table 1
Classification of photo-Fenton processes at neutral pH by ligand, pollutant, pH, radiation source, nature of the aqueous matrix, species analyzed, and eventual comparison with conventional photo-Fenton (DW = Distilled Water; SFW = Surface Water; WW = Wastewater; TW = Tap Water; STW = Synthetic Water).

Ligand	Pollutants	pH	Radiation source	Nature of the aqueous matrix	Analysis	Intermediates	Comparison with photo-Fenton	Ref	TOC removal (%)	Pollutant removal (%)
EDTA EDDS NTA	EDTA	4.5–8.5	lamp	DW	EDTA consumption	Formaldehyde, ethylenediglycine, iminodiacetic acid	NO	[79]	53 (pH = 6.9)	up to 100
	EDTA	4.0–9.0	UVC –UVA	DW	EDTA	ND	NO	[51]	NA	NA
	EDTA	7.4	UVB–UVA, natural sunlight	SFW	EDTA	ND	NO	[46]	NA	NA
	Sulfamethoxazole (SMX)	8.0	UVA	DW	SMX, TOC, H ₂ O ₂	ND	NO	[24]	NA	~80
	EDTA, EDDS	3.1–7.0	UVB–UVA, natural sunlight	DW and SFW	EDTA, EDDS	ND	YES	[80]	NA	up to 100
	Bisphenol A, nitrobenzene	3.7–8.7	UV–vis	DW	Bisphenol A, nitrobenzene	ND	YES	[47]	NA	up to 100
	Pharmaceuticals	7.6–8.3	Natural sunlight	WW	Pharmaceuticals, DOC, H ₂ O ₂	ND	NO	[78]	NA	~100
	Estradiol	3.1–8.0	UVB–UVA	DW	Estradiol	ND	NO	[77]	NA	up to 98
	Pharmaceuticals	6.0–7.0	Natural sunlight	WW	Pharmaceuticals, DOC, H ₂ O ₂	ND	NO	[30]	NA	>90
	Emerging contaminants	7.6–8.3	Natural sunlight	WW	EC, H ₂ O ₂	ND	YES	[36]	NA	>95
	Pharmaceuticals	7.3–8.5	Natural sunlight	WW	Pharmaceuticals, DOC, TOC, Total iron, H ₂ O ₂	ND	NO	[113]	NA	~90
	4-chlorophenol (4-CP)	4.0–8.0	UVA	DW	4-CP	Quinones	YES	[48]	NA	up to 82
	Citrate	3.0–7.0	UVA	DW	Citrate	ND	NO	[103]	NA	NA
	Dyes	1.0–9.0	UVB	DW	Dyes	ND	YES	[101]	NA	NA
CITRATE	Arsenic	6.5–8.0	UVA	TW and STW	Arsenic	ND	YES	[102]	NA	80–90
	Tebuthiuron (TBH)	2.5–7.5	Natural sunlight	DW	TBH, TOC	ND	YES	[82]	~20 (pH = 7.5)	~78 (pH = 6.0)
	Diclofenac (DCF)	5.0–8.0	Natural sunlight	WW, DW	DCF, TOC	ND	YES	[99]	77 (pH = 7)	62 (pH = 5–7)
	Pharmaceuticals	6.0–7.0	Natural sunlight	WW	Pharmaceuticals, DOC, H ₂ O ₂	ND	NO	[30]	NA	>90
	Oxytetracycline (OTC)	3.0–6.0	UV–vis, sunlight	DW, WW	OTC, DOC, H ₂ O ₂	ND	NO	[89]	~40 (pH = 5)	>98
	Anisole, nitrobenzene	4.5–8.0	Vis	DW	Anisole, nitrobenzene	ND	NO	[21]	NA	~75 (pH = 6.3)
	Cresol	2.9–6.4	UVA	DW	Cresol	ND	YES	[45]	NA	~50 (pH = 6.44)
	Atrazine	3.5–8.6	UVA–Vis	DW	Atrazine	ND	YES	[52]	NA	NA
	Alachlor	2.0–8.0	UVA–Vis	DW	Alachlor, TOC, nitrate	organic intermediates	YES	[98]	~65 (pH = 5)	up to 100~65 (pH = 7)
	Diphenhydramine (DPD)	3.0–9.0	UVA–Vis	DW	DPD	organic intermediates	NO	[100]	NA	~90 (pH = 6)

OXALATE	Dyes	2.0–6.0	UVC	DW	Dyes	ND	YES	[83]	NA	NA
	Trimethoprim (TMP), Sulfamethoxazole (SMX)	2.8–6.5	Natural and artificial sunlight	DW	TMP, SMX, DOC	ND	YES	[75]	up to 40% (pH = 6.5)	up to 98 (pH = 6.5)
	Sulfadiazine(SDZ), sulfathiazole(STZ)	2.5–6.0	UVA	DW	SDZ, STZ, TOC	ND	YES	[88]	no significant mineralization ~25 (pH = 6)	up to 100
	Dyes	2.8–6.0	Natural and artificial sunlight	WW	DOC, COD, Total dissolved iron, discolouration	carboxylic acids	YES	[74]	~25 (pH = 6)	NA
	Dyes	6.0	Natural sunlight	WW	TOC, COD, BOD	organic acids	NO	[84]	up to 77	NA
	Winery wastewater	>3.5	Natural sunlight	WW	TOC	ND	YES	[92]	up to 61 (pH = 3.5)	NA
	Textile wastewater	2.8–5.0	Natural sunlight	WW	DOC, COD, Total dissolved iron	ND	YES	[85]	~58 (pH = 5)	up to 100
	Reactive Black 5 (RB5)	2.0–8.0	UVC	DW	RB5, TOC	ND	YES	[86]	~30 (pH = 5)	~80 (pH = 6)
	Phenolic compounds	5.6	Natural sunlight	WW	COD, BOD, Phenols	ND	NO	[93]	up to 85	up to 100
	Bisphenol (BPA)	3.0–8.0	UVA-Vis	DW	BPA	quinones, phenols	YES	[94]	23.9 (pH = 3.5)	~10 (pH = 6)
	2,4-dichlorophenoxyacetic acid (2,4-D)	1.2–7.4	UVB-A	DW	2,4-D	ND		[90]	NA	82(pH = 7.4), 98 (pH = 6)
	Phenolic compounds	2.0–6.0	Natural sunlight	DW	Phenolic compounds, TOC	ND	NO	[95]	94 (pH = 4)	100 (pH = 4)
	Black B (RBB)	4.0–6.0	UVA	DW	RBB	ND	YES	[87]	71 (pH = 5)	73 (pH = 6), 99.8 (pH = 5)
	Pharmaceuticals (ECs)	4.0–6.1	Natural sunlight	WW	ECs, DOC, H ₂ O ₂	ND	YES	[76]	30	98–100
	Diclofenac (DCF)	5.0–6.0	Artificial and natural sunlight	DW	DCF, DOC	organic acids	YES	[55]	63 (pH = 6)	100 (pH = 6)
	Oxytetracycline (OTC)	3.0–6.0	UV-vis, sunlight	DW, WW	OTC, DOC, H ₂ O ₂	ND	NO	[89]	~32 (pH = 6)	>98
	Anisole, nitrobenzene	4.5–8.0	Vis	DW	Anisole, nitrobenzene	ND	NO	[21]	NA	NA
	4-Chlorophenol (4-CP)	1.5–11	UV	DW	4-CP, TOC	ND	NO	[96]	5 (pH = 7)	95 (pH = 7)
	2,4-dichlorophenoxyacetic acid (2,4-D)	5.0	Artificial sunlight	DW	2,4-D	ND	NO	[91]	NA	95.9
	Arsenic(III)	3.0–7.0	UV-vis	DW	As(III)	ND	YES	[97]	NA	NA

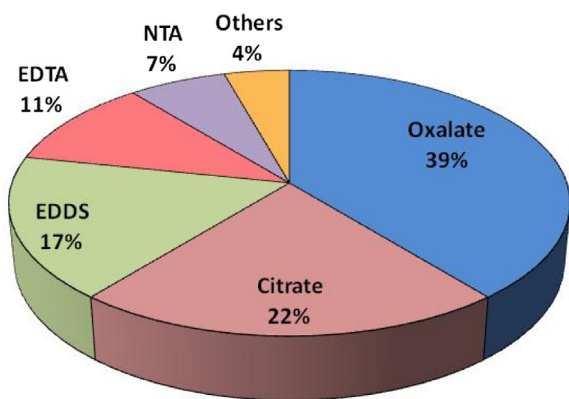


Fig. 2. Relative occurrence of different ligands in the review literature: oxalate, citrate, ethylenediamine-N,N'-disuccinic acid (EDDS), ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and other minor ligands.

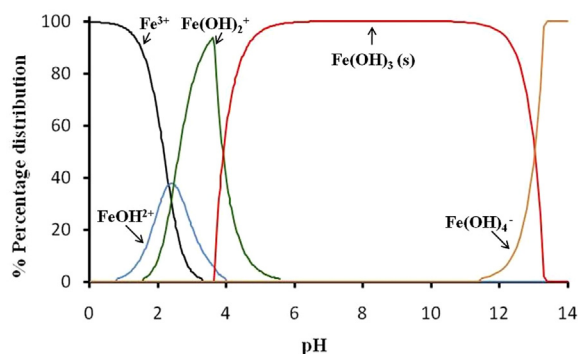


Fig. 3. Speciation diagram of ferric hydroxyl-species as a function of pH for a solution containing $1.0 \cdot 10^{-5}$ M of Fe(III) at 25 °C. The speciation diagram was obtained by MINEQL+ software.

not considered for the present review as well as the investigation of the possibility to carry out heterogeneous photo-Fenton processes. Fig. 2 shows a diagram indicating the relative incidence of each ligand in the papers considered for the present work. In Table 1 the main indications found in these papers are reported.

2. Discussion

2.1. Conventional photo-Fenton

The starting point for the present work was obviously represented by conventional photo-Fenton process, since it is considered as a clear reference in the most part of the papers analyzed.

Such process is performed in presence of Fe(III) ions, whose concentration is low in agreement with their catalytic role, and hydrogen peroxide. Generally, pH values of about 3.0, $\text{H}_2\text{O}_2/\text{Fe(III)}$ molar ratios of 2–150, and $\text{H}_2\text{O}_2/\text{COD}$ (Chemical Oxygen Demand) molar ratios of 1–3.5 [38–40] are required. Moreover, photo-Fenton process can be performed under UV-A artificial lamps ($\lambda > 300$ nm) or solar light irradiation.

These conditions promote the formation of FeOH^{2+} , capable of photolyzing upon absorption of UV/solar radiation.

The quantum yield for Fe(II) formation is wavelength dependent [41–43] and reported equal to 0.14–0.19 at 313 nm and 0.017 at 360 nm [41].

Fig. 3 shows the speciation of iron in water. By starting from a pH of about 1, free Fe(III) concentration reduces giving rise to the formation of both FeOH^{2+} and Fe(OH)_2^+ aquo-complexes. For pH values between 2.0 and 3.0, FeOH^{2+} reaches the highest percentage,

thus ensuring the maximum system reactivity. It is clear that the system reactivity decreases with increasing pH above the value of 3.0, due to a decrease in concentration of both photoactive FeOH^{2+} and dissolved iron. Indeed, for pH higher than 4.0 dissolved iron precipitates as ferric hydroxide.

The papers surveyed for the present review aimed at disclosing the correlation between system reactivity and pH.

2.2. Most commonly used chelating agents and iron(III) speciation

The speciation diagrams of Fe(III) in the presence of different ligands are reported in Fig. 4a–f. These diagrams were obtained for the present work by running MINEQL+ software [107]. When Fe(III) is dissolved in aqueous solution in presence of one of the ligands reported in Fig. 2, soluble Fe(III)-containing compounds are formed at pH higher than 3.0. Fig. 4a indicates that, when EDTA is adopted, the formation of soluble complexes (i.e., FeEDTA) allows to shift to basic pH values with no precipitation of Fe(III). The use of citrate, NTA, oxalate, and EDDS may even make Fe(III) available until near-neutral pH by forming soluble complexes, as reported in Fig. 4b–f, respectively.

As shown in Fig. 4e, the addition of tartrate to the aqueous solution does not significantly shift the precipitation of Fe(III) to higher values of pH. Moreover, the Fe(III)-tartrate complex is not present at pH higher than 5.0. For this reason, the use of tartrate in photo-Fenton processes at near neutral pH was not exhaustively considered for the present literature review.

2.3. Optical absorption properties of iron(III)-ligand complexes

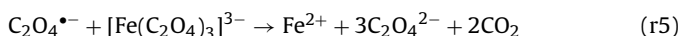
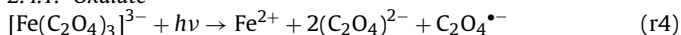
Generally speaking, each system exhibits different light absorption properties at varying pH according to the resulting complex speciation. A few data on the relationship between light absorption and pH for the systems of interest were found for the present survey. Fig. 5 shows a comparison of the optical absorption properties of systems containing FeOH^{2+} , Fe(III)-oxalate-, and Fe(III)-citrate-complexes. The diagrams indicate that Fe(III)-oxalate and Fe(III)-citrate species can absorb light more intensely than FeOH^{2+} , with an extension of absorption in the visible range (up to $\lambda = 440$ nm). These observations point out that the formation of Fe(III)-ligand complexes allows the system to more efficiently exploit the solar radiation. As shown in Fig. 6, a moderate increase in visible absorption also applies to Fe(III)-EDTA complexes.

2.4. Mechanisms of reaction

The capability of a single ligand to form strong complexes with Fe(III) is essential to prevent the precipitation of Fe(III) as iron hydroxide. However, in order to ensure an efficient degradation of organic pollutants, Fe(III) complexes should not only absorb light in the UV-vis range but also undergo photolytic decomposition.

In the absence of photolytic decomposition the system appears to be unreactive. The photolytic decomposition can be broadly represented by reaction r_3 . In other words, the ligand gives one electron to the metal allowing its reduction. This is the starting step of a complex reaction network which is summarized in reactions r_4 – r_9 for oxalate.

2.4.1. Oxalate



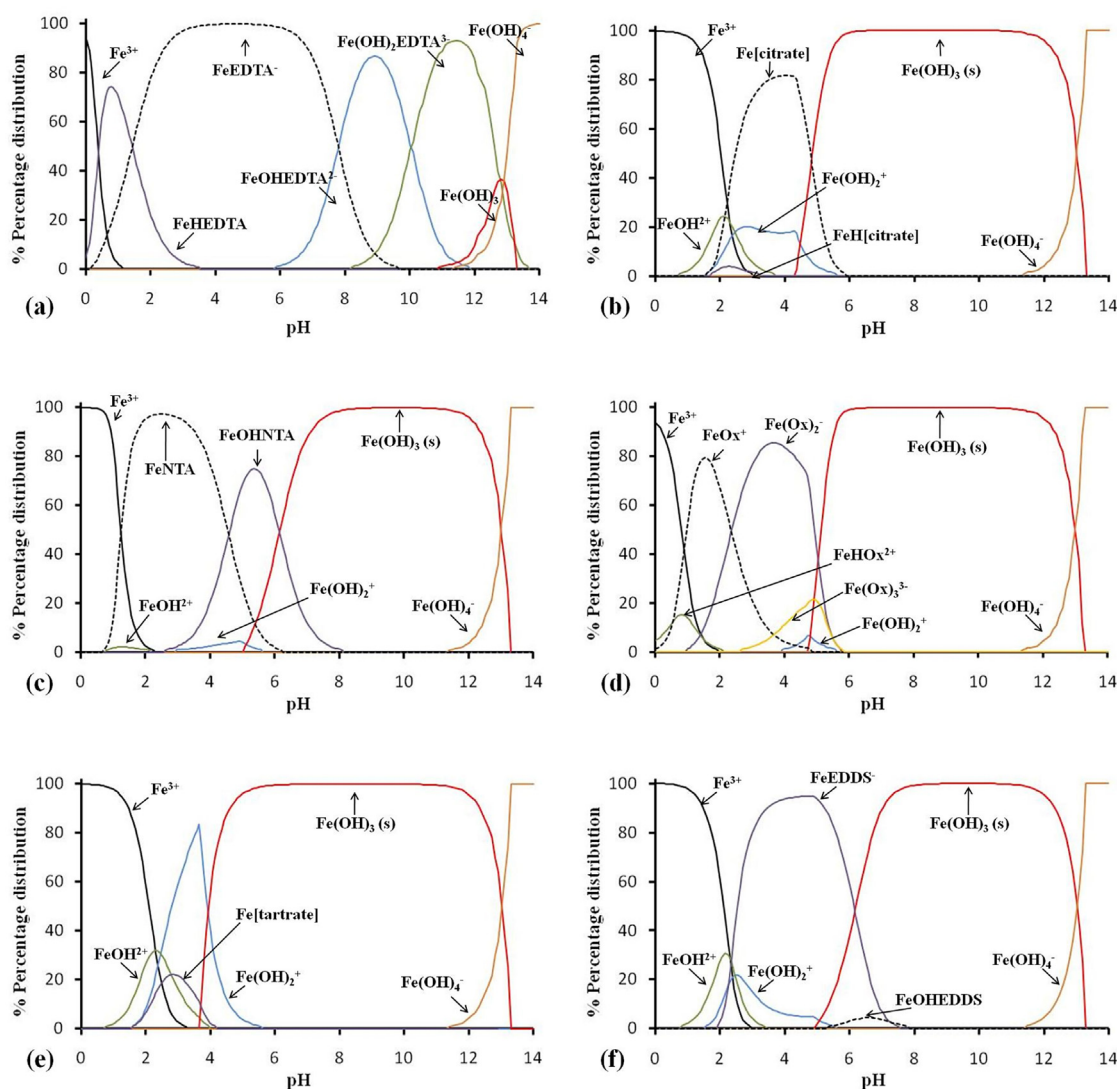
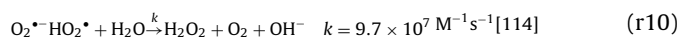
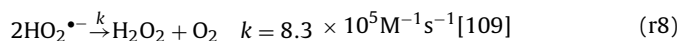
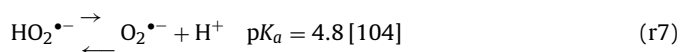
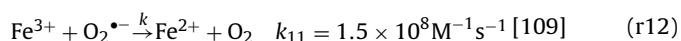
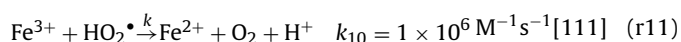


Fig. 4. Speciation diagrams of ferric complexes as a function of pH for a solution at $T = 25^\circ\text{C}$ in the presence of $1.0 \times 10^{-5}\text{ M}$ of Fe(III), $1.0 \times 10^{-5}\text{ M}$ of EDTA (a), $1.0 \times 10^{-5}\text{ M}$ of citrate (b), $1.0 \times 10^{-5}\text{ M}$ of NTA (c), $3.0 \times 10^{-5}\text{ M}$ of oxalate (d), $1.0 \times 10^{-5}\text{ M}$ of tartrate (e), and $1.0 \times 10^{-5}\text{ M}$ of EDDS (f). The speciation diagrams were obtained by MINEQL⁺ software.



The mechanism proposed also takes into account the participation of oxygen to the oxidation process leading to the formation of superoxide radical anion (r7) and hydrogen peroxide (r8, r10). The presence of oxygen is reported to positively affect the pollutant degradation [47], since the formation of superoxide radical anions through reaction r6 promotes the reduction of Fe(III) to Fe(II) at neutral pH, as stated in reactions r11 and r12:



Weller et al. [49] found that $\text{Fe}(\text{Ox})_2^-$ complex has a higher quantum yield at 313 nm for Fe(II) generation than $\text{Fe}(\text{Ox})_3^{3-}$.

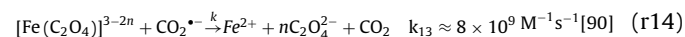
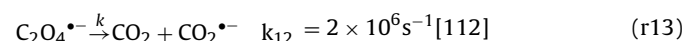
Table 2

Quantum yields for bis- and tris- (oxalato)ferrate(III) [49].

	313 nm	366 nm	436 nm
$[\text{Fe}(\text{Ox})_2]^-$	≥ 1.23	1.17	1.4
$[\text{Fe}(\text{Ox})_3]^{3-}$	0.12	0.91	1.0

The values of quantum yields of photolysis for bis- and tris- (oxalato)ferrate(III) complexes at three different wavelengths are reported in Table 2.

They also demonstrated the dependence of the quantum yield on secondary reactions (i.e., the reaction between carboxyl radical and unphotolyzed ferrioxalate complexes reported in reactions r13 and r14), which were affected by the initial concentration of Fe(III) and the light intensity:



A mechanism similar to that proposed for ferrioxalate is reported also for other ligands, as reported in the following para-

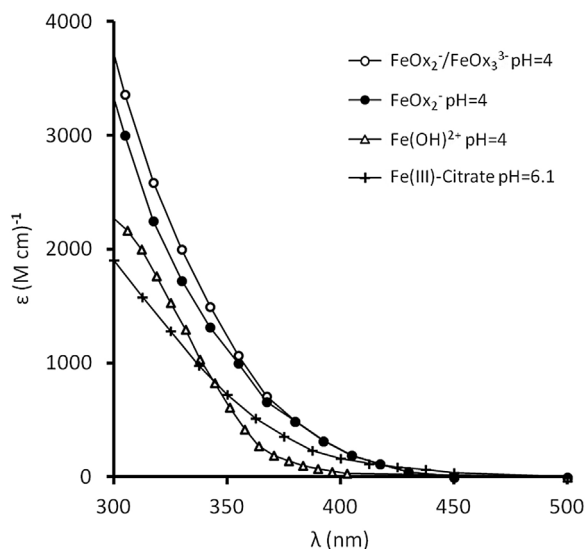


Fig. 5. Molar absorption coefficients of chelated species: (○) $\text{FeOx}_2^-/\text{FeOx}_3^{3-}$ for $\text{Fe(III):oxalate} = 1:12$ at $\text{pH} = 4$ [44]; (●) FeOx_2^- for $\text{Fe(III):oxalate} = 1:3$ at $\text{pH} = 4$ [44]; (△) Fe(OH)^{2+} at $\text{pH} = 4$ [41]; (+) Fe(III)-citrate for $\text{Fe(III):citrate} = 1:1$ at $\text{pH} = 6.1$ [45].

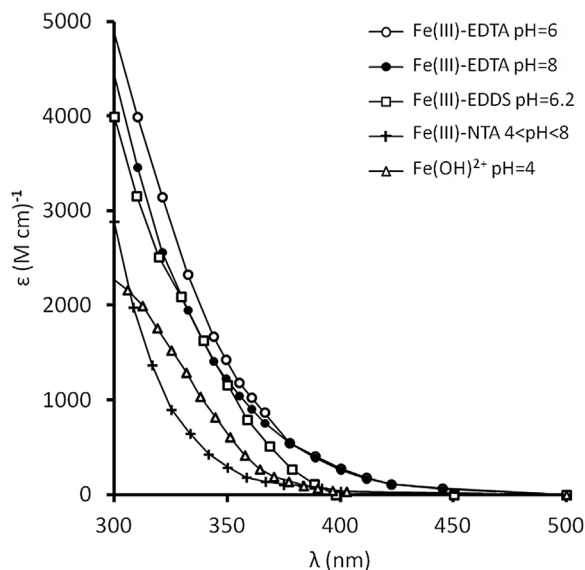


Fig. 6. Molar absorption coefficients of chelated species: (○) Fe(III)-EDTA for $\text{Fe(III):EDTA} = 1:1$ at $\text{pH} = 6$ [46]; (●) Fe(III)-EDTA for $\text{Fe(III):EDTA} = 1:1$ at $\text{pH} = 8$ [46]; (□) Fe(III)-EDDS for $\text{Fe(III):EDDS} = 1:1$ at $\text{pH} = 6.2$ [47]; (△) Fe(OH)^{2+} at $\text{pH} = 4$ [41]; (+) Fe(III)-NTA for $\text{Fe(III):NTA} = 1:1$ in the range $4 < \text{pH} < 8$ [48].

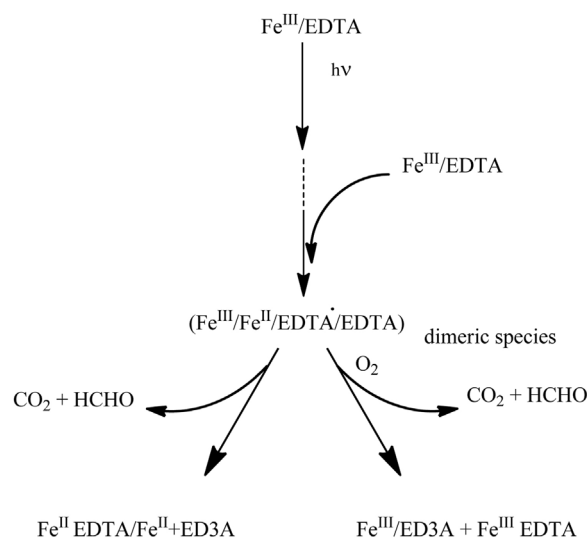
graphs. Further information on the reported mechanisms and the kinetic constants of the reactions can be found in [90] and [108].

2.4.2. EDDS

Wu et al. [50] reported a reaction mechanism for Fe(II) formation by photolysis of Fe(III)-EDDS complexes (r_{15} – r_{16}).



They evaluated an “average” quantum yield of Fe(II) produced by photolysis of Fe(III)-EDDS complexes between 290 and 400 nm at different pH. The Authors supposed that the rate of Fe(II) formation is equal to the degradation rate of Fe(III)-EDDS complexes. The average quantum yields reported are 0.09, 0.11, and 0.10 at pH 4.0, 6.0, and 8.6, respectively.



ED3A = ethylenediamine triacetic acid

Fig. 7. Possible reaction pathways for photolysis of Fe(III)-EDTA complex [51].

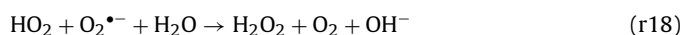
Table 3

Quantum yields for Fe(III)-EDTA photolysis [51].

λ [nm]	pH	O_2 present	O_2 absent
313	4	0.05 ± 0.006	0.09 ± 0.010
	9	0.01 ± 0.002	0.06 ± 0.007
365	4	0.02 ± 0.002	0.06 ± 0.005
	9	0.01 ± 0.001	0.04 ± 0.003
405	4	–	0.05 ± 0.006
	9	–	–

In a second paper from some of the Authors [114], the rate of OH radical formation from the photochemical processes was evaluated according to r_7 , r_9 , r_{10} , r_{15} , and r_{16} .

Li et al., [77] reported the quantum yield of hydroxyl radicals formation as a pH function. It is remarkable that it increases with pH, in contrast with what reported in the absence of ligands. The reported values for $[\text{Fe(III)-EDDS}] = 10^{-4}$ M at $\lambda = 265$ nm are $\Phi_{\text{OH}} = 0.0025, 0.0091, 0.019, 0.025, 0.034, 0.051, \text{ and } 0.069$ at $\text{pH} = 3.0, 4.0, 5.1, 6.0, 7.0, 8.0, 9.0$, respectively. At $\text{pH} > 4.8$ (pK_a of the couple $\text{HO}_2/\text{O}_2^{\bullet-}$), $\text{O}_2^{\bullet-}$ is the dominant reactive oxygen species and the hydrogen peroxide formation rate increases of an order of magnitude according to reactions r_{17} and r_{18} .



The same authors reported quantum yields of OH radicals formation as a function of wavelength for $[\text{Fe(III)-EDDS}] = 10^{-4}$ M at pH 6.0 ($\Phi_{\text{OH}} = 0.025, 0.037, \text{ and } 0.040$ at 365, 313 and 296 nm, respectively).

As reported by Zhang et al. [105], in the presence of hydrogen peroxide Fe(III)-EDDS complexes are also degraded because of the reaction of EDDS with OH radicals ($2.48 \pm 0.43 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at $\text{pH} = 8$). A comparison with NTA complexes is reported in the below paragraph on NTA.

2.4.3. EDTA

Kocot and coworkers [51] reported the quantum yield values for the photolysis of Fe(III)-EDTA complex. As shown in Table 3,

Table 4

Quantum yields of Fe(II) formation from photolysis of Fe(III)-NTA complexes in the presence of 4-chlorophenol [48].

pH	313 nm	325 nm
4.0	0.46	0.28
6.0	0.16	0.04

they depend on pH, radiation wavelength, and the presence of dissolved oxygen in solution. Such dependences suggest the existence of complex reaction pathways through which the photolytic process develops.

As reported in Fig. 7, the same Authors found that after a first electron transfer from EDTA to Fe(III) which is reduced to Fe(II), a dimeric species containing both Fe(II) and Fe(III) forms. Such species may undergo either (i) a simple decomposition accompanied by Fe(III) reduction and EDTA oxidation, under deoxygenated conditions, or (ii) a reaction with O₂ leading to ferric ion regeneration and partial oxidation of EDTA in the presence of dissolved oxygen.

2.4.4. NTA

The complex between Fe(III) and NTA is capable of photolyzing upon radiation absorption for $\lambda > 300$ nm, leading to the formation of Fe(II) ions.

Two mechanisms were proposed for this photolytic process by Abida et al. [48]. The first one is showed in Fig. 8 and applies for $\lambda > 345$ nm. A redox reaction between Fe(III) and carboxylate group occurs, leading to the formation of Fe(II) and carboxyl radical, the latter undergoing a fast decarboxylation. The hydrogen radical coming from this reaction leads to the formation with oxygen of OH radical and hydrogen peroxide, which is capable to reoxidizes Fe(II).

The second mechanism proposed by the Authors applies to photolysis of Fe(III)-NTA complexes for wavelengths between 310 and 345 nm and is shown in Fig. 9. For shorter wavelengths, water ligand transfers an electron to Fe(III) causing its reduction with the contemporary formation of OH radicals and of a proton ion. The last species makes possible the oxidation of the organic substrate through the participation of oxygen molecule and formation of radical carbonate anion.

The Authors also estimated the quantum yields of Fe(II) formation at two different pH values (4.0 and 6.0) and wavelengths (325 and 313 nm). Such values, determined in the presence of 4-chlorophenol, are reported in Table 4. Lower values were found in the absence of 4-chlorophenol.

According to Zhang et al. [105], a comparison with Fe(III)-EDDS complexes degradation in the presence of hydrogen peroxide (lamp emission from 200 to 530 nm) showed that Fe(III)-NTA degradation was slightly faster than Fe(III)-EDDS under the same conditions, even though the reactivity of NTA with OH radicals is much lower ($4.77 \pm 0.24 \text{ M}^{-1} \text{ s}^{-1}$ at pH=8). The effect was explained with the formation of μ -peroxo adducts with hydrogen peroxide (H₂O₂-Fe(III)-NTA). These adducts can be converted to Fe(IV)-oxo species. The mechanism seems to be more efficient for NTA than EDDS complexes.

2.4.5. Citrate

Ou et al. [52] investigated the photodegradation of atrazine in the presence of Fe(III) and citrate in aqueous solution using a Xenon lamp as radiation source in the pH range 3.5–8.6. They demonstrated that, in the presence of high citrate concentrations, the photodegradation rate increases due to the formation of Fe(III)-citrate complexes capable of absorbing light and undergoing photolytic processes which reduce Fe(III). Table 5 shows the quantum yields of Fe(II) formation by photolysis of Fe(III)-citrate

Table 5

Quantum yields of Fe(II) formation from by photolysis of Fe(III)-citrate complexes.

pH	Citrate:Fe(III)	366 nm	436 nm	References
2.7	5	0.28	–	[53]
2.9	167	0.17	–	[53]
3.5	10	–	0.23	[52]
4.0	1	–	0.28	[54]
4.0	5	0.45	–	[53]
4.0	5	–	0.28	[54]
4.0	10	–	0.24	[54]
5.0	1	–	0.25	[54]
6.0	1	–	0.21	[54]

complexes reported by several authors at different pH and wavelengths.

As a general comment to all the complexes examined, only few literature indications are reported dealing with further chelating abilities of the radical species formed after the single electron transfer from the ligand to the metal. For example, De Luca et al. [24] suggest that in a system containing an almost stoichiometric ratio of Fe(III) and EDTA, only 26% of the metal precipitates after a substrate (i.e., sulphamethoxazole) conversion of about 70%. Such results demonstrate that even the oxidized form of EDDS has complexing ability towards iron(III).

Wang et al. [106] also pointed out a decrease in the quantum yield of Fe(II) formation when increasing the pH from 2.0 up to 5.0, but they do not report their values in the case of citrate.

2.5. Iron/ligand ratio

The addition of chelating species to aqueous waste streams causes an increase in the initial value of TOC. This appears to be in contradiction with the general aims of AOPs application, which seek to remove pollutants of concern from wastewaters and reduce TOC by achieving high degrees of mineralization. It is important to note that for each of the aforementioned chelating species a different initial concentration is required, depending on pH, Fe(III) concentration, and stability constant for the complexation of Fe(III). Different initial increases in TOC depending on the chelating species adopted are therefore expected. As the system reactivity depends on the concentration of Fe(III) complexes, the possibility of exploiting all metal ions in solution and preventing their precipitation as hydroxides is of great interest. A careful control of iron/ligand ratio is essential to achieve this result. De Luca et al. [24] reported that a Fe(III):ligand ratio of 1:1 does not always ensure complete complexation of Fe(III). These Authors investigated the effect of adding EDTA, NTA, oxalic acid, and tartaric acid to the solution: they demonstrated that only in the presence of EDTA an almost complete chelation of Fe(III) was achieved with a Fe(III):EDTA ratio of 1:1. They also found that an increase in ligand concentration beyond the value required for complete complexation of Fe(III) favorably affects the system reactivity. This result was related to the ability of excess ligand to complex iron ions released from complexes photolyzed or attacked by hydroxyl radicals. The same Authors pointed out that hydroxyl radicals attack Fe(III)-ligand complexes with consequent breakage of complexes and iron release in solution. Iron released precipitates, thus reducing the catalytic activity. Therefore, the reactivity of metal-organic chelates with hydroxyl radicals is crucial to monitor process efficiency.

As regards oxalic acid, De Luca et al. [24] tested the iron/ligand molar ratio usually reported in scientific studies (i.e., oxalic acid:iron = 10:1) with the aim of assessing the catalytic effect resulting by adopting a correct molar ratio. Only 30% of pollutant removal (i.e., sulfamethoxazole) was recorded for the 1:10 iron/ligand molar ratio system, whereas an increase up to 70% of pollutant removal was observed with a 1:20 iron/ligand molar ratio.

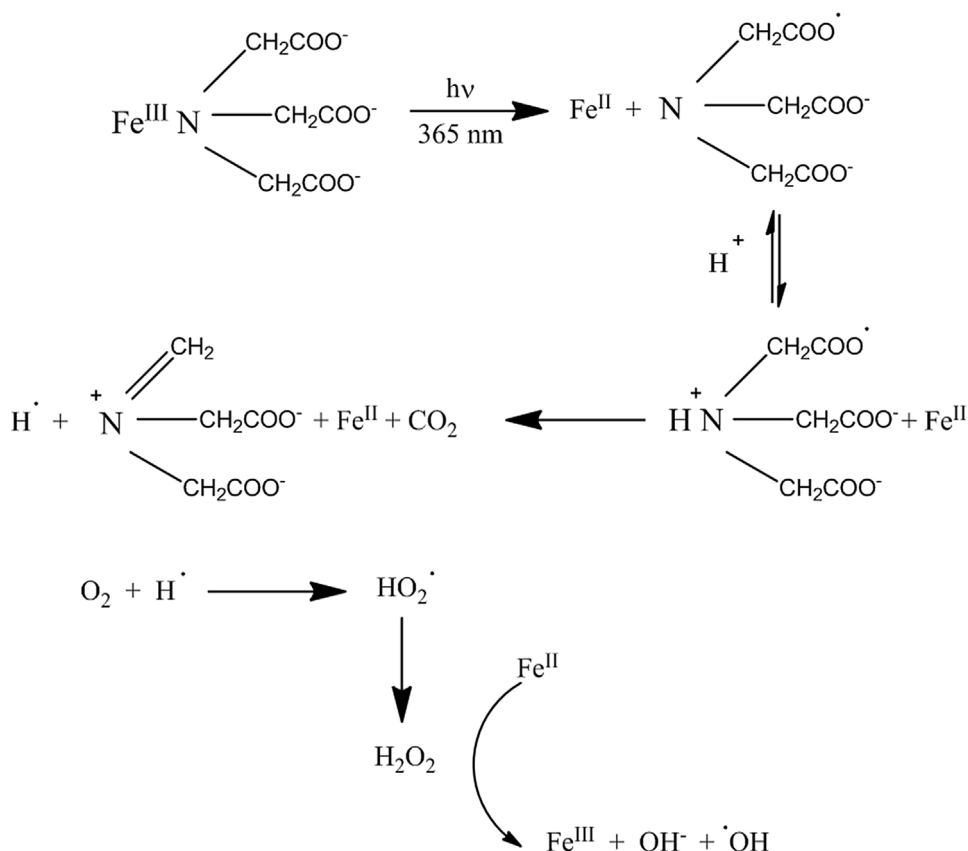


Fig. 8. Photolysis of Fe(III)-NTA complexes for $\lambda > 345 \text{ nm}$ [48].

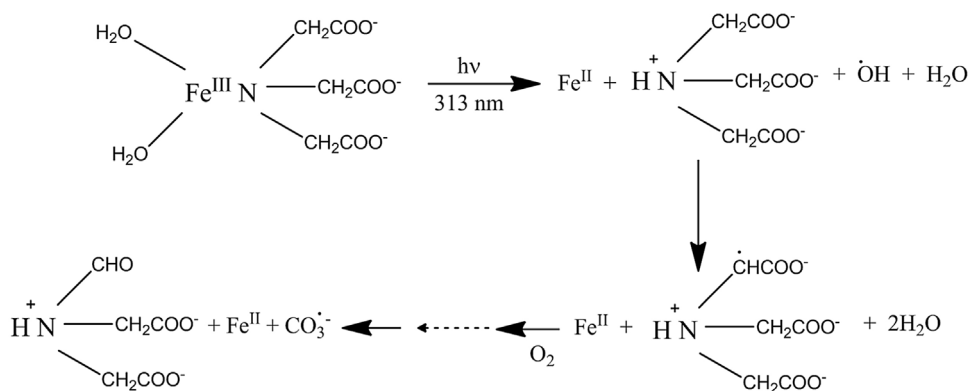


Fig. 9. Photolysis of Fe(III)-NTA complexes for wavelengths between 310 and 345 nm [48].

Souza and coworkers [55] also investigated the effect of the Fe(III):ligand ratio in the case of oxalate. They observed a complete degradation of diclofenac at pH 6.0, with a mineralization degree of 63% after 90 min. The Fe(III):oxalate molar ratio of 1:9 they used at pH 6.0 is three times the ratio required to get the same results at pH = 5.0.

2.6. Biodegradation and toxicity

Since small traces of ligands are commonly detected in civil and industrial wastewaters, photo-Fenton processes at neutral pH require addition of complexing agents. Incomplete oxidation of ligands in wastewater treatment plants may accidentally occur. It is therefore crucial to collect biodegradability and toxicity indications on these compounds.

High concentrations of ligands in wastewaters or surface waters can remobilize heavy metals from sludges and sediments, respectively, and affect planktonic algae growth, thus increasing the risk of eutrophication. No acute toxicity effects to many forms of life were recorded on ligands in surface waters [56]. On the other hand, little information on long-term exposure effects is reported in literature.

Overall, the environmental fate of chelating agents depends on several parameters, such as their chemical speciation, their interaction with metals, water hardness, and pH [57].

2.6.1. EDTA

EDTA has been referred to as a poorly biodegradable and recalcitrant organic compound by several authors [33,58]. Its persistence in the environment stimulated the adoption of other aminopolycarboxylic acids (APCAs), such as NTA and EDDS. However, the

photodegradation products of Fe(III)-EDTA complexes show a relatively high biodegradability [59].

When high amounts of EDTA are ingested by mammals, metal excretion and membrane permeability of cells can be compromised [56].

The LC_{50} values for fish toxicity (i.e., the value of EDTA concentration accounting for 50% of mortality within a predetermined time period) strongly depend on the way in which EDTA is present. LC_{50} values in the range of 100–450 mg/L are reported for sodium salt EDTA and free EDTA. Substantially lower toxicity is related to EDTA-calcium complex (LC_{50} = 2000 mg/L), due to unchanged levels of water hardness when adding this compound to the system [57]. In general, increasing values of water hardness are related to decreasing levels of toxicity [60,61].

Further ecotoxicological data found for the present literature review revealed that EDTA is relatively non-toxic to *Daphnia magna* in case of acute exposure (LC_{50} = 60 mg/L), but nothing is reported on its chronic impact [60].

High concentrations of EDTA have toxic effects on bacteria for metal chelation on their exterior membrane [56]. EDTA may also enhance the toxic effect on bacteria of other xenobiotics, such as tributyltin [60,62].

Due to its high nitrogen content (10%), EDTA is of serious concern for its direct and indirect contribution to eutrophication. In particular, EDTA is reported to be vital for the growth of some algae, such as *Microcystis aeruginosa*, *Dunaliella*, and *Amphidinium* [60,63,64].

EDTA is also able to release Fe(III) ions from their phosphate-bound form in sediments, thus remobilizing phosphates in surface waters and indirectly contributing to eutrophication [60].

2.6.2. NTA

NTA is easily biodegraded by microbial populations in surface waters. The kinetics for NTA biodegradation is strongly affected by temperature and dissolved oxygen concentration, whereas water hardness appears to have negligible influence [65].

From acute and chronic toxicity tests over a wide range of freshwater and marine organisms, Anderson et al. [65] found that NTA exhibits toxic effects only if its concentration is equal or exceeds the concentration of divalent metal ions in the system. In particular, by comparing LC_{50} values, NTA results to be almost one order of magnitude less toxic to marine species than to freshwater ones. This difference in toxicity could be ascribed to the complexation of NTA with cations in seawater. As regards chronic toxicity, No Observed Effect Concentration (NOEC) values result approximately one order of magnitude higher than actual concentrations of NTA in surface water, thus reducing the possibility of severe environmental risks.

No direct eutrophication effects are related to NTA, even when considering its expected maximum level in surface waters.

The potential for NTA to mobilize heavy metals from sediments is negligible, taking into account the realistic concentrations of NTA in the environment.

A low acute toxicity of Fe(III)-NTA and its photolysis products towards *Vibrio Fischeri* has been reported [105].

2.6.3. EDDS and natural low molecular weight organic acids (NLMWOA)

EDDS shows different biodegradability rates depending on its optical isomer (SS-, RS- and RR-isomers).

Vandevivere et al. [66] reported that free [S,S]-EDDS is promptly biodegraded, whereas the degradation of metal-[S,S]-EDDS complexes depends on the metal type. In particular, Cu, Ni, Co, and Hg complexes remain almost undegraded.

Several authors [67,68] indicated EDDS a sustainable substitute for EDTA in environmental applications, such as soil washing and chelated enhanced phytoremediation [69–71].

Jaworska et al. [72] measured the EC_{50} values for fishes and *Daphnia* (i.e., the EDDS concentration sufficient to obtain 50% of a maximum effect to the test population) and deduced a low toxicity of [S,S]-EDDS to these organisms (EC_{50} > 1000 mg/L).

Zhang et al. [105] pointed out the low toxicity of EDDS and Fe(III)-EDDS complexes towards *Vibrio Fischeri* (12.7% and 12.1% inhibition of bioluminescence, respectively). However they found that the toxicity of Fe(III)-EDDS solutions increased during the photolysis of the complex, ascribing the effect to N-(2-aminoethyl) aspartic acid formation, even though they ignore the occurrence of synergistic effects. In the same paper a comparison with Fe(III)-NTA complexes is reported, the latter showing a lower toxicity.

With regard to natural low molecular weight organic acids, such as oxalic acid and DL-tartaric acid (TA), no concerns were raised about their application, as they are not considered as recalcitrant to biodegradation or toxic to aquatic fauna.

2.7. Criteria for choosing chelating agents and operating conditions

According to what reported above, the following arguments have to be considered in choosing chelating species and operating conditions for an efficient and sustainable photo-Fenton process at near neutral pH.

- 1) The addition of chelating agents to wastewaters always leads to an increase in TOC and operating costs. Therefore, the addition should be limited to the minimum amount ensuring the highest removal efficiency of pollutants or the maximum TOC reduction.
- 2) If the photolytic process is performed by means of UV–vis lamps (that is a valuable complementary option on cloudy days at low solar radiation), the calculation of the energy per order (EE/O) proposed by Bolton et al. [73] represents a reliable strategy to evaluate the process efficiency and compare performances of different chelators.

Following this approach, a rational choice of organic ligand should be made by selecting the species ensuring the lowest cost related to its addition and a minimal initial increase in TOC. De Luca et al. [24] reported a comparison among EDTA, NTA, oxalic acid, and tartaric acid for the removal of sulfamethoxazole from aqueous solutions at pH 7.0. They concluded that the use of NTA, at the Fe(III):NTA molar ratio of 1:1.5, appears to be the most appropriate.

However, biodegradability and toxicity evaluations of the selected compound and its complexes are essential.

2.8. Examples of application

2.8.1. Oxalate

A possible exploitation of this reaction network was introduced by Doumic et al. [74], who applied the photo-Fenton/ferrioxalate process to the treatment of simulated textile wastewater at varying pH. Their results indicated a decrease in system reactivity with increasing of pH above 4.8. A speciation diagram of ferric complexes as a function of pH proposed by the Authors is reported in Fig. 4d. As shown in the diagram, iron is present in the form of Fe(III) and ferric di-oxalato species up to the pH value of 4.0. The formation of Fe(OH)₃ for pH higher than 4.0 is evidenced by MINEQL+ modeling of a system at ambient temperature (30 °C) and ionic strength of 0.3 M, containing 7.16×10^{-4} M of Fe(III) (40 mg Fe(III)/L) and 2.15×10^{-3} M of oxalic acid ($189 \text{ mg C}_2\text{H}_2\text{O}_4 \text{ L}^{-1}$) [74]. However, a direct comparison between Figs. 4 d and 3 allows to understand the role of oxalate in iron hydroxide precipitation at higher pH and the importance of the formation of photolytically reactive tris-oxalate instead of unreactive Fe(OH)₂⁺ x at increasing pH. The use of modified photo-Fenton processes in the presence

of oxalate for treating dye-containing wastewaters was studied by several authors, as shown in Table 1 [18,83–87].

Dias et al. [75] studied an updating of the photo-Fenton process through the addition of oxalate. An enhancement in the reaction efficiency for the removal of antibiotics (trimethoprim and sulfamethoxazole) at pH 5.0 was recorded with an iron concentration of 5.0 mg/L. Ferrioxalate complexes seem capable of reducing the formation of iron(III)-antibiotics species which delayed Fe(III) reduction.

Klamerth et al. [76] investigated the possibility to use a modified photo-Fenton process on the effluents of a municipal wastewater treatment plant. In the absence of any compound capable to form complexes with Fe(III), oxalate was added and the removal of 15 emerging contaminants was followed. Appreciable removal efficiencies of target species were achieved, although a low pH was recorded in the final water stream.

Souza et al. [55] proposed a photo-Fenton process in the presence of oxalate for the degradation of diclofenac at near neutral pH (5.0 and 6.0), under the solar radiation. The precipitation of iron hydroxide was avoided and the concentration of total iron was kept below the limits for the discharge to surface water.

Further studies dealing with the treatment of antibiotics [88,89] and herbicides [90,91] in wastewaters by means of photo-Fenton/ferrioxalate processes were found. In addition, Table 1 reports other examples of application of such processes for the treatment of streams containing phenolic compounds [92–96], aromatic compounds [21], and arsenic [97].

2.8.2. EDDS

Li et al. [77] investigated the photochemical effect of Fe(III)-EDDS complexes on hydroxyl radical formation and degradation of 17-estradiol. The Authors found that the quantum yield of hydroxyl radical formation by photolysis of Fe(III)-EDDS complexes is higher at higher pH values between 3.0 and 9.0. Similarly, 17-estradiol was degraded by photolysis of Fe(III)-EDDS complexes, which depends on pH and concentrations of Fe(III)-EDDS complex, Fe(III), and O_2 .

The Fe(III)-EDDS system was used by Huang and coworkers [47] to study the degradation of bisphenol A. The Authors found that EDDS can stabilize Fe(III) in aqueous solution between pH 3.0 and 9.0 by preventing its precipitation. They also reported that the addition of EDDS helps achieve high degradation degrees of organic species over a wide range of pH.

The photo-Fenton process in the presence of EDDS was also investigated by Klamerth et al. [78] for the removal of micropollutants from Municipal Wastewater Treatment Plant (MWTP) effluents at neutral pH. The rapid degradation of selected contaminants (i.e., acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole, and triclosan) was recorded under solar radiation. Furthermore, the Authors proposed an interesting attempt to disinfect such effluents through the photo-Fenton process investigated

Klamerth et al. [36] compared two different solar photo-Fenton processes for treating real MWTP effluents containing over 60 different contaminants: (i) conventional photo-Fenton at pH = 3 and (ii) modified photo-Fenton (with either humic acids at neutral pH or EDDS) at low Fe(III) and H_2O_2 starting concentrations. In both processes, removal efficiencies of about 95% were achieved. However, conventional photo-Fenton at pH = 3 had the drawback that the stream must be previously acidified and neutralized thereafter, with an increase in salinity and costs. Photo-Fenton with humic acids had the additional drawback that pH decreased during the process. The most favorable process was photo-Fenton modified with EDDS, which helped maintain a constant pH in the neutral range. The main disadvantage of this option was the treatment cost, since EDDS was also degraded during the process.

Miralles-Cuevas et al. [30] compared the efficiencies of EDDS and citrate in pilot-plant-scale photo-Fenton experiments at neutral pH for two cases: (i) direct treatment of a MWTP effluent containing five pharmaceuticals (carbamazepine, flumequine, ibuprofen, ofloxacin and sulfamethoxazole) and (ii) treatment of a concentrate stream generated by nanofiltration (NF). In both cases, the pharmaceuticals were efficiently removed (>90%). The advantage of using NF was that higher pharmaceutical concentrations can be treated by photo-Fenton. Fe(III):complex best ratios for treating NF concentrate with 0.2 mM Fe(III) at neutral pH were found to be 1:2 for EDDS and 1:5 for citrate. However, the Authors concluded that EDDS was the more efficient ligand for complexing iron.

De la Obra et al. [113] investigated the solar photo-Fenton removal of five pharmaceuticals in the secondary effluent of a municipal wastewater treatment plant with Fe(III)-EDDS complexes at circumneutral pH. Two different reactor setups were compared: raceway pond reactors (RPRs) and compound parabolic collectors (CPC) reactors. The pharmaceutical removal efficiency in RPRs (1.07 mg/kJ) was four times the value achieved in CPC reactors (0.26 mg/kJ). The effect of varying the liquid depth in RPRs was also investigated: an optical value of 15 cm was assessed.

2.8.3. EDTA

De Luca et al. [24] investigated a system at pH 7, containing 0.294 mM of hydrogen peroxide, 0.089 mM of Fe(III), and an Fe(III):EDTA molar ratio of 1:1. They observed remarkable results for the removal of sulfamethoxazole from aqueous solution under UV irradiation ($\lambda = 350\text{--}400\text{ nm}$). Fe(III)-EDTA complexes showed far more efficient results than complexes between Fe(III) and oxalic acid or tartaric acid. Moreover, according to the same Authors the reactivity of Fe(III)-EDTA complexes is comparable to that of Fe(III)-nitrilotriacetate complexes.

Table 1 reports several examples [46,51,79,80] in which the photodegradation of Fe(III)-EDTA complexes was studied. Although no removal of further organic species was investigated, such papers throw light on the reaction mechanism of photo-Fenton processes at neutral and near neutral pH.

2.8.4. NTA

Abida et al. [48] demonstrated the ability of Fe(III)-NTA complexes to promote the oxidation of 4-chlorophenol in the presence of oxygen. In deaerated conditions, no oxidation of 4-chlorophenol was recorded, whereas the photolysis of Fe(III)-NTA complexes was not affected by the presence of oxygen. The addition of a radical scavenger (i.e., isopropanol) to the system completely inhibited the oxidation of the pollutant.

The degradation of carbamazepine in the presence of Fe(III)-nitrilotriacetate complexes was investigated by Sun and coworkers [81] in a wide pH range 5.0–9.0. The following optimal conditions were identified: Fe(III) = 10^{-4} M , H_2O_2 :Fe(III) = 155:1, NTA:Fe(III) = 3:1, pH (7.0), and ambient temperature. An apparent pseudo-first order kinetic constant of $0.0419 (\pm 0.002)\text{ min}^{-1}$ was estimated at pH = 7.0. This constant was found to increase for pH changes between 5.0 and 9.0. An interesting comparison between NTA and EDDS complexes in removing the acid extractable organic fraction from oil sands process-affected water at natural pH is proposed by Zhang et al. [105]. They found that the UV-NTA-Fenton process is more efficient in removing a higher amount of organics (66.8% highest removal; H_2O_2 dose: 5.88 mM) compared to UV-EDDS-Fenton (50% highest removal; H_2O_2 dose: 4.41 mM). This is mainly ascribed to the lower reactivity of NTA with HO radicals.

2.8.5. Citrate

As reported above, Ou and coworkers [52] examined the degradation of atrazine in aqueous solutions containing Fe(III) and citrate

in a wide pH range. At pH 5.4, they recorded an increase in photodegradation rate with increasing citrate concentration.

Silva and coworkers [82] investigated the role of Fe(III)-citrate complexes in a solar photo-Fenton process for the removal of the herbicide tebuthiuron (TBH) from aqueous solutions at circumneutral pH. A higher removal degree was achieved by the Fe(III)-citrate system at pH 6.0 with respect to the Fe(III) system at pH = 2.5. In particular, the following operating conditions were adopted: TBH = 0.5 mM; $\text{Fe}(\text{NO}_3)_3 = \text{C}_6\text{H}_8\text{O}_7 = 1.0 \text{ mM}$; $\text{H}_2\text{O}_2 = 10 \text{ mM}$. It is worthy to observe that the addition of citrate at pH 2.5 resulted in the fastest substrate removal. The improved system reactivity observed after adding citrate may be ascribed to the higher molar absorption coefficients values of Fe(III)-citrate complexes in a wide pH range with respect to FeOH^{2+} , as shown in Fig. 5.

The photo-Fenton degradation of the herbicide alachlor in the presence of citrate solution was successfully achieved by Katsumata et al. [98] at neutral pH. Various applications of such systems to the treatment of selected pharmaceuticals [30,89,99,100], dyes [101], and arsenic in wastewaters were found. The photolytic degradation of Fe(III)-citrate complexes was investigated by several papers at different pH values, as summarized in Table 1.

3. Conclusions

The addition of selected polycarboxylates and aminopolycarboxylates to aqueous waste streams in the presence of iron(III), hydrogen peroxide, and UV-vis radiation allows to extend conventional photo-Fenton processes to neutral or near neutral pH. This literature survey indicated a growing interest among researchers in this approach due to its ability to overcome the severe limitations of conventional photo-Fenton, which are essentially related to expensive pH adjustments. It is the current opinion that this approach may boost the use of conventional photo-Fenton in real applications. Following the literature indications, it can be stated that an ideal Fe(III)-ligand for conventional photo-Fenton processes at near neutral or neutral pH should be capable of:

- Strongly complexing Fe(III) ions in order to form stable species and prevent Fe(III) precipitation as hydroxide;
- Significantly absorbing UV-vis radiation;
- Photolyzing upon radiation absorption and generating Fe(II) ions.

The results of the present survey indicated that in principle many organic species, such as oxalate, tartrate, citrate, EDTA, NTA and EDDS, show the abovementioned properties.

It is clear that, although all these species allow to extend the pH range of conventional photo-Fenton, a proper choice of chelator and operating conditions should take into account the costs of both the ligand and the energy of the lamp. The initial increase in TOC after chelator addition and both the biodegradability and ecotoxicity of the species formed should be also evaluated.

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